



Kinetic sorption of contaminants of emerging concern by a palygorskite-montmorillonite filter medium



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HIGHLIGHTS

- BPA, CMZ & CIP reached equilibrium sorption onto palygorskite within 3, 5 and 16 h.
- Sorption capacities were inversely related to palygorskite granule size.
- Pseudo-second-order model fit all sorption data well.
- Langmuir kinetic rate constants were theoretically derived for predictive capacity.
- Model fits indicated fast surface sorption followed by intraparticle diffusion.

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ABSTRACT

Kinetic sorption of bisphenol A (BPA), carbamazepine (CMZ) and ciprofloxacin (CIP) by three palygorskite-montmorillonite (Pal-Mt) granule sizes was studied. For BPA, CMZ and CIP, apparent sorption equilibrium was reached within about 3, 5 and 16 h, respectively. The highest and the lowest sorption capacities were by the small and the large granule sizes, respectively. Experimental results were compared to various sorption kinetics models to gain insights regarding the sorption processes and achieve a predictive capacity. The pseudo-second order (PSO) and the Elovich models performed the best while the pseudo-first order (PFO) model was only adequate for CMZ. The intraparticle-diffusion (IPD) model showed a two-step linear plot of BPA, CMZ and CIP sorption versus square root of time that was indicative of surface-sorption followed by IPD as a rate-limiting process before equilibrium was reached. Using the pseudo-first order (PFO) and the pseudo-second order (PSO) rate constants combined with previously-established Langmuir equilibrium sorption models, the kinetic sorption (k_a) and desorption (k_d) Langmuir kinetic rate constants were theoretically calculated for BPA and CIP. Kinetic sorption was then simulated using these theoretically calculated k_a and k_d values, and the simulations were compared to the observed behavior. The simulations fit the observed sorbed concentrations better during the early part of the experiments; the observed sorption during later times occurred more slowly than expected, supporting the hypothesis that IPD becomes a rate-limiting process during the course of the experiment.

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1. Introduction

Contamination of groundwater and surface water by pharmaceuticals and endocrine disrupting compounds (EDCs) is an emergent concern (Kolpin et al., 2002; Strock et al., 2010; Lapworth et al., 2012; Zhang et al., 2012). Sewage treatment plants (STPs) are the

main gateway of these compounds to the natural environment mainly due to inefficiencies in the existing treatment technologies (Kolpin et al., 2002; Zhang et al., 2008; Miège et al., 2009; Lapworth et al., 2012). Consequently, environmental contamination by pharmaceuticals and EDCs is widespread not only due to the low removal percentage of these compounds by STPs but also due to the persistent nature of the compounds including their resistance to bio- and photo-degradation (Jos et al., 2003; Strock et al., 2010; Lapworth et al., 2012). Many studies have therefore focused on identifying and/or synthesizing and testing various materials that

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may prove to be robust and inexpensive alternatives or supplementary materials to existing STP technologies (Xu et al., 2012a, 2012b; Li et al., 2014). Sorption is one of the most commonly-employed methods at STPs and municipal drinking-water treatment plants to remove organic contaminants from solution supplemented by converting them into less-harmful compounds (Alkan et al., 2008; Pan et al., 2008; Yu et al., 2009).

A potentially natural and inexpensive sorbent is a palygorskite-montmorillonite (Pal-Mt) clay which has a documented record of applicability as an excellent sorbent for various types of organic compounds (Galan, 1996; Chang et al., 2009a, 2009b; Nasedkin et al., 2009; Berhane et al., 2015). For instance, Chang et al. (2009a) found that tetracycline sorption was endothermic following a Langmuir sorption isotherm with a maximum sorption capacity of 99 mg g⁻¹, where pronounced effects of pH and ionic strength on sorption were observed. Pal-Mt clay also has the advantage of being potentially recyclable with heat treatment. Palygorskite clay materials have long been recognized as adsorbent materials for a variety of applications (e.g., Galan, 1996). These materials are well recognized as being complex mineral mixtures with palygorskite-sepiolite minerals of variable structures (e.g., Guggenheim and Krekeler, 2011; Krekeler and Guggenheim, 2008; Krekeler et al., 2004, 2005).

Previous experiments have shown Pal-Mt clay to be an effective sorbent with the EDC, bisphenol A (BPA), and the pharmaceuticals, carbamazepine (CMZ) and ciprofloxacin (CIP) (Berhane et al., 2015, 2016). While the exact mechanisms are not definitively known, the adsorption mechanism of CIP is likely due to the electrostatic interaction of RR'NH₂⁺ with SiO⁻ unprotonated silanol groups or hydrogen bonding with SiOH groups. CMZ and BPA can only undergo hydrogen bonding with SiOH groups through the respective nitrogen atoms and OH groups. There is evidence of strong interaction of other protonated amine organics such as diphenhydramine and atenolol. Dyes with multiple amine groups show strong interactions with Pal-Mt, similar to what we have found with these same dyes on plain silica used for high-performance liquid chromatography columns.

To optimize contaminant removal capacities at STPs by different materials, it is important to understand the dynamics and the rate controlling processes of mass transfer at the sorbent-sorbate interface (Gürses et al., 2006; Alkan et al., 2008; Plazinski et al., 2009; Liu et al., 2014). This includes but is not limited to, investigating the contact time required between the contaminants in solution and the sorbent to reach apparent or true equilibrium conditions (Ho and McKay, 1999; Alkan et al., 2008). For instance, when the rate of sorption is fast, sorption equilibrium is reached within a short period of time, thereby, comparatively, a short hydraulic retention time is needed allowing STPs to treat large volumes of sewage influent (Ho and McKay, 1999; Gürses et al., 2006). This is important as many STPs need to cope with large and seasonally-fluctuating volumes of sewage influent. Also, previous studies indicated sorption hysteresis between these emerging contaminants and Pal-Mt clay (Berhane et al., 2015, 2016). One possible explanation of this hysteresis effect is non-equilibrium sorption. Therefore, kinetic sorption needs to be investigated and mathematical models of kinetic sorption need to be developed so that they can be used in conjunction with mass-transport models to adequately predict and manage the treatment of pharmaceuticals and EDCs within a sorption medium.

The Lagergren pseudo-first-order (PFO), the pseudo-second-order (PSO) and the intra-particle diffusion (IPD) kinetic sorption models are some of the most commonly-used models quantifying the removal of heavy metals and organic contaminants from solution as a function of time (Ho and McKay, 1999; Plazinski et al., 2009; Yu et al., 2009). In addition, the Elovich model has been

recently widely used to characterize sorption of organic molecules by solid materials (Ho, 2006b; Qiu et al., 2009). The advantage of the aforementioned four models is their simplicity and the ease with which they can be fitted to the observed data. In addition, the IPD model has the potential to lend insight regarding the processes underlying sorption. However, distinguishing between sorption mechanisms based on the model fitting is difficult as the differences in the measures of fit are often marginal (Plazinski et al., 2009). Moreover, these models lack a true predictive capacity in that the fitted parameter values are often strongly dependent on the experimental initial conditions (Plazinski et al., 2009). All sorption rate coefficients, equilibrium or kinetic, can be dependent on such external factors as solution pH, temperature and ionic strength. In addition, however, the PFO rate constant, and especially the PSO rate constant, can be strongly dependent on the applied initial concentration (Plazinski et al., 2009). The dependence could be quantified and used to make predictions of sorption times in a static situation (Plazinski et al., 2009), but this dependence reduces the degree to which the PFO and PSO models can be used to make predictions in a transport setting where the concentrations entering different sections of a filter medium would be constantly changing. Ultimately, the goal of sorption experiments in the context of filter-media investigations is to produce a predictive model that can be incorporated into a contaminant fate and transport model. Most contaminant transport and fate models incorporate linear, Freundlich or Langmuir kinetic or equilibrium sorption models. Azizian (2004) and Liu and Shen (2008) have shown how the PFO and PSO models can be derived directly from the Langmuir model given certain assumptions. To increase the predictive applicability of these sorption investigations we have used those derivations to determine the Langmuir kinetic sorption rate constants from the PFO and PSO model fits. Descriptions of the PFO, PSO, Elovich and IPD models are provided at the end of the Materials and Methods section. A new approach to the Langmuir kinetic sorption model and its relation to the PFO and PSO models is provided at the beginning of the Results and Discussion section.

In this study, the kinetic sorption of three emerging contaminants onto Pal-Mt clay was investigated: one EDC, BPA, and two pharmaceuticals, CMZ and CIP (Table 1). The compounds were chosen based on a combination of two or more of the following factors: low retention capacity at STPs, low bio- and photo-degradability potentials, impact to aquatic ecosystem health and differences in their chemical properties leading to expected differences in their sorption characteristics. They were also selected for this study because their equilibrium sorption behavior with Pal-Mt clay was previously quantified for a variety of Pal-Mt granule sizes, solution temperatures, pH values and ionic strengths (Berhane et al., 2015, 2016). All of the four kinetic sorption models were explored, and based on these models, a predictive kinetic Langmuir sorption model was derived.

The specific objectives of this study were:

- 1) Investigation of the time-dependent sorption of the three emergent contaminants, BPA, CMZ and CIP and fitting of observed sorption to appropriate kinetic sorption models.
- 2) Evaluation of the effect of Pal-Mt granule size (0.3–0.6 mm, 1.7–2.0 mm and about 2.8 mm) on kinetic sorption including the time required of the three compounds to reach sorption equilibrium onto the Pal-Mt. Higher flow rates and hence more sewage influent treatment could be achieved using the larger sizes; however, the smaller sizes have more reactive sites per unit mass of sorbent and therefore result in more contaminant retention per unit mass of sorbent.
- 3) For the compounds that follow a Langmuir equilibrium isotherm, BPA and CIP (Berhane et al., 2016), a further objective

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